LOWER WILLAMETTE GROUP

PORTLAND HARBOR RI/FS

REMEDIAL INVESTIGATION REPORT

APPENDIX D1.5
COMPARISON AND USE OF PCB AROCLOR AND CONGENER DATA

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APPENDIX D1.5 COMPARISON AND USE OF PCB AROCLOR AND CONGENER DATA

D1.5.1 Introduction

Depending on the objectives of the specific investigation, two types of PCB analyses were used for Portland Harbor RI samples: 1) identification and quantification of PCBs as Aroclors using gas chromatography with electron capture detection (most commonly by EPA method 8082), and 2) direct analysis of PCB congeners. PCB congener analysis is generally performed using high-resolution gas chromatography with high-resolution mass spectrometry (EPA method 1668A); however, some data using method 8082 for congeners are included in the Portland Harbor SCRA Database (Tetra Tech 2006). In order to provide a clear representation of the patterns and trends of PCBs in the Study Area, PCB totals based on both congeners and Aroclors are displayed together on maps and graphs in Section 5 for sediments and biota. As described below, the PCB congener analysis is preferred when available and should be given greater weight in any analysis. However, both sets of data can be useful for generally assessing the spatial distribution of PCBs and combining both types of data allows presentation of the most complete and representative data set.

The numbers of available samples from the Study Area and adjacent and upstream areas that were analyzed for Aroclors and PCB congeners are as follows:

Matrix	Number of Samples Analyzed for Aroclors	Number of Samples Analyzed for PCB Congeners	Number of Samples Analyzed for Both Aroclors and PCB Congeners
Surface Sediment	1,514	299	290
Subsurface Sediment	1,539	151	149
Biota	170	369	89
Sediment Trap Samples	48	52	48

This appendix provides a description of the analytical methods used for Aroclors and PCB congeners with supporting information to provide context for these methods, followed by a comparison and evaluation of the total PCB data obtained by the two methods.

D1.5.2 PCB Analysis Methods

In North America the primary source of PCBs to the environment was the industrial use of Aroclors (Sather et al. 2001). Aroclor® was the trade name for various PCB mixtures produced by the Monsanto Corporation. The nine most commonly analyzed Aroclors are Aroclors 1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262, and 1268. The last two numbers in the Aroclor name indicate the percent of chlorine, by weight, in the technical mixture. Aroclor 1016 is an exception to this rule, with 41 percent chlorine by weight. The PCB congener (and homolog group) distribution of each Aroclor is unique (Newman et al. 1998), as shown in Figure 5.1-34.

Historically, most PCB analyses have been based on Aroclors, reflecting the primary source of the PCBs. Aroclor identification is generally performed by comparing the chromatogram of a sample to chromatograms of Aroclor standards. Each Aroclor has a PCB congener composition that yields a characteristic pattern of peaks. If the PCB pattern observed in the sample matches an Aroclor standard, the Aroclor is identified as present in the sample and quantified.

Several factors complicate Aroclor analyses, including "weathering," differences between Aroclor formulations and production lots, and the presence of multiple Aroclors and chemical interferents. "Weathering" can modify Aroclor patterns in samples, including processes such as partitioning, photolysis, and biodegradation. In general, the more chlorinated the PCB congener, the more persistent it is in the environment. However, various "weathering" processes may remove less chlorinated or more highly chlorinated congeners (Erickson 1997); conversely transport processes may enrich some congeners. Additionally, other "weathering" processes may selectively remove congeners from an Aroclor pattern without production of new congeners (Frame et al. 1996). Photolytic and anaerobic microbial dechlorination can lead to the presence of congeners not originally present in Aroclors. The congener composition of PCBs found in environmental samples frequently differs greatly from the source Aroclors (Sather et al. 2003), and these changes can affect the ability of the laboratory to accurately identify or quantify the PCBs.

Analyses of the PCB congener distributions in Aroclors have also shown that different production lots of an Aroclor can have different congener compositions (Frame et al. 1996). The differences in homolog distributions between the lots were relatively minor; however, differences in PCB congener distributions were more significant. These differences can introduce error to the quantification of Aroclors to the extent that the standards and released Aroclors are dissimilar in PCB composition.

It is also common in environmental samples to encounter interferences from non-PCB sources or multiple Aroclors. The presence of such background interferences or effects of "weathering," or both, can make it difficult to differentiate between Aroclors with similar chlorine content, such as Aroclors 1016 and 1242, 1242 and 1248, or 1260 and 1262. The co-occurrence of Aroclors in a sample can also make identification of Aroclor patterns difficult (EPA 2007).

In addition, the presence of multiple Aroclors, weathered PCBs, and interferences may cause the laboratory to elevate detection limits for affected Aroclors. This was the case with a number of samples collected for the Portland Harbor RI/FS. For the RI data set, non-detected Aroclors are treated as zero in the summation to calculate total PCB Aroclors (if no Aroclors are detected, then the highest detection limit is used for the total PCB detection limit). If PCBs are present at a concentration below the elevated Aroclor detection limit but above the regular detection limit, the total Aroclor value may underestimate total PCBs.

Quantification of PCBs as Aroclors is based on the assumption that the PCB congeners in the sample are present in the same ratio as in the Aroclor that is used as a standard. As a result, when a sample has undergone substantial modification due to "weathering," or when two or more source Aroclors are present that have congeners in common, the quantification of the PCBs as Aroclors may not fully reflect the concentration of PCB congeners present in the sample. The bias may be high or low, depending on whether the peaks used to quantify the Aroclors represent congeners that are depleted or enriched relative to their concentration in the original source Aroclor. The magnitude and direction of the bias are also affected by the extent to which the ratio between peaks used to quantify the Aroclors and the remaining peaks has been altered. This is a source of error that is inherent in the method and can result in differences between total PCBs analyzed as Aroclors or by direct measurement of congeners. Nevertheless, Aroclor analyses are based on established methodology and are widely used. Total Aroclor concentrations are considered to be sufficiently reliable for RI/FS purposes.

The analysis of PCB congeners is more expensive and time-consuming than Aroclor analysis, but it is less affected by the factors described above. Each congener of interest is identified and quantified separately. When all 209 congeners are analyzed, any congeners that were not initially present in the Aroclors, or originated from other sources, are also accounted for. PCB congener analysis is usually performed using mass spectrometry, which is better able to differentiate PCBs from non-PCB interferences and is therefore less influenced by the presence of other chemicals. Additionally, the method employed for the analysis of PCB congeners is more sensitive than the Aroclor method and will detect congeners at lower levels than the Aroclor method. Examples of this sensitivity are seen in the RI data set, which includes 90 samples (65 sediments, 18 sediment trap samples, and 7 biota) with detections for PCB congeners when Aroclors were undetected.

The total PCB congener and total Aroclor data for sediments and biota were combined into a single data set to facilitate characterization of PCBs in the Study Area. These total PCB data were used to create Maps 5.1-1 and 5.1-2a–m. Due to the laboratory method and analytical considerations discussed above (and with the exception noted below), the total PCB data set includes the result for total PCB congeners for each sample when available, and the result for total Aroclors when no total PCB congener data are available. However, total Aroclor data were selected to represent total PCBs for Round 2A beach sediment samples even though congener analyses were also conducted, because the beach samples were only analyzed for coplanar PCB congeners, which constitute a small fraction of Aroclor-related congeners. Congener analyses for the remaining LWG sediment samples included all 209 congeners. Total PCB data for the Study Area are available for 1,184 surface and 1,325 subsurface samples. Most of the PCB data are based on Aroclor analyses (Tables 5.1-1 and 5.1-2).

D1.5.3 Comparison of Total Aroclor and Total PCB Congener Concentrations

The total Aroclor and total PCB congener results were evaluated to determine the comparability of data obtained by the two PCB methods. Scatter plots displaying PCB concentrations by river mile within the Study Area are provided in Figures D1.5-1a–b. In general, the high total Aroclor concentrations correspond well with the high total congener concentrations spatially; the two data sets are consistent in their representation of the distribution of total PCBs and identification of areas of high PCB concentrations.

The concentrations obtained using the two PCB methods were compared by regressing the total congener concentration on the total Aroclor concentration for samples that were analyzed by both methods, as shown in Figure D1.5-2. Data were log-transformed to satisfy the assumptions of normality for linear regression analysis. For sediments, data were available from RM 1.4 to 18.8 and Multnomah Channel, and for tissues, data were available from RM 2.4 to above the falls. Sediment trap data were available from RM 1.8 to 15. The numbers of samples used in these plots are fewer than the sample counts tabulated above, as samples with non-detects are excluded. Biota (coefficient of determination [r^2] = 0.87) showed the best correlation, with subsurface sediments showing the poorest (r^2 = 0.48). For all data assessed together, r^2 was 0.70. The slopes of the regression formulae are less than 1 for all matrices except sediment traps, indicating that the total Aroclor data provide a higher total PCB estimate overall than total PCB congener data. This is not unexpected as "weathering" processes or the presence of multiple Aroclors or chemical interferences can lead to a high bias in total Aroclor results.

The regressions of PCB Aroclor and congener concentrations were not significantly different for surface and subsurface sediment data (P = 0.42). These two data sets were analyzed together (N = 360) and their regression (r^2 = 0.88, P < 0.01) statistically compared to the 1:1 line (Figure D1.5-3). This analysis indicated that total Aroclor data tend to overpredict (using the log-log linear regression) total PCB congeners in concentrations below ~750 μg/kg (total PCB Aroclors) and may result in underprediction above this threshold.

For the surface sediment data, an in-depth Simulation-Extrapolation procedure was performed to assess the effect of measurement error of Aroclor concentrations on the regression-predicted values of total PCB congener concentrations. The methods and results of this analysis are presented in Attachment D1.5.1. In short, this analysis highlights increasing uncertainty in the predictive power of a linear model between total Aroclor and congeners in surface sediment with increasing total Aroclor concentrations.

D1.5.4 QC Sample Variability

Several types of quality control (QC) samples were collected to assess field and laboratory precision, including field duplicates (i.e., post-homogenization split samples) for Aroclors and PCB congeners, laboratory duplicates (separate analyses of the same

sample) for PCB congener analyses, and matrix spikes and matrix spike duplicates (MS/MSDs) for Aroclor analyses. The variability of these QC samples provides a measure of the extent to which the variability observed in the Aroclor and congener data may be attributed to field and laboratory procedures. Scatter plots of field and laboratory duplicate concentrations are provided in Figures D1.5-4 and D1.5-5a–b. These figures include samples collected by the LWG for which Aroclors and PCB congeners were both detected. A summary of the relative percent difference values for environmental and QC samples is provided in Table D1.5-1.

Among the different levels of replication illustrated in Figures D1.5-4 through D1.5-5a–b and summarized in Table D1.5-1, laboratory duplicate, MS/MSD, and field duplicate results all showed better correlation overall than total PCBs analyzed as Aroclors and congeners in the same samples. One would expect the correlation to be highest between MS/MSDs and laboratory duplicates because the same sample jar and the same laboratory and method are used for these analyses. Field duplicates were collected in different jars, as were the samples for the two different PCB analyses for this investigation, but the same laboratory analyzed the field duplicates, often in the same processing batch. Samples for Aroclor and PCB congener analyses, however, were analyzed from different jars and by different laboratories using different extraction and cleanup procedures. This combination of conditions would be expected to yield greater variability between Aroclor and PCB congener results than MS/MSDs, laboratory duplicates, and field duplicates for each of the PCB analyses. Nonetheless, it can be seen in Table D1.5-1 that a sizable portion of the measured variability can be attributed to the environmental sample collection and analysis process.

While total Aroclor and total congener results generally track each other across the entire data set, there is a small subset of samples where the totals measured by the two methods diverge dramatically. Aroclors and PCB congeners were detected in a total of 535 samples, and the total Aroclor and total congener concentrations differed by more than a factor of 10 in 11 (or 2 percent) of these samples. These samples are listed in Table D1.5-2. For these 11 samples, the differences between the results by the two PCB methods are markedly greater than would be expected based on differences between the two PCB methodologies.

To investigate these differences, the laboratory data were examined for all samples with greater than ten-fold differences between reported total PCB Aroclor and congener concentrations, and for surface sediment samples with differences greater than five-fold, to determine whether a chemical interference or laboratory error could be identified. Although no obvious errors or consistent problems were identified, at least a portion of the differences between results could be attributed to one or more of the factors discussed above that commonly affect Aroclor quantification. These included chemical interferences, including TPH, PAHs, and DDx; the presence of multiple Aroclors, which affected the quantification of individual Aroclors; the presence of weathered PCBs with low chlorination levels that don't resemble an Aroclor; and PCB concentrations close to the reporting limit, where quantification is less precise than at

higher concentrations. For most of these samples, however, these interferences did not appear to be sufficient to fully account for the large differences found between the total Aroclor and total PCB congener results. The differences are also likely to be the result of sample inhomogeneities related to the small-scale distribution of PCBs in the sediment, possibly including the presence of particles of materials such as paint, soot, or other organic particles, droplets, or colloids with associated PCBs.

Measurement error in Aroclor concentrations also increases the uncertainty of a linear regression prediction of congener concentrations (for example, in samples where only Aroclors were measured). This effect was examined and quantified using a simulation-extrapolation procedure detailed in Attachment D1.5.1.

D1.5.5 Conclusion

PCB congener data better represent total PCB concentrations than Aroclor data, as the congener method is less affected by "weathering," non-PCB interferences, and subjective Aroclor identifications. However, both methods represent the total PCB concentrations well, and measured total PCB concentrations are fairly comparable between methods in most cases (especially when measurement error is considered). Overall, results for total PCB congeners and Aroclors agreed within a factor of 2 for 72 percent of samples and within a factor of 4 for 90 percent of the samples. As the Portland Harbor SCRA database includes both total PCB congener results and total Aroclor results, it is useful to combine them to represent the spatial distribution of PCBs in the Study Area as fully as possible. In addition, the analysis of sediment data indicated that total Aroclor data overpredict total PCB congeners in concentrations below ~750 µg/kg total Aroclors and may result in underprediction above this threshold. Therefore, the use of Aroclor data to represent total PCBs will result in similar or more conservative site management decisions with a much larger spatial and temporal coverage than the use of congener data alone.

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